

## CLAIMS:

1. A method for joining a substrate having a first surface to an object having a second surface comprising the steps of:

5 (i) applying an effective amount of a curable adhesive composition to the first surface of the substrate, the second surface of the object or to both surfaces, wherein the adhesive comprises

(a) an effective amount of an organoborane amine complex initiator and

10 (b) one or more monomers, oligomers, polymers or mixtures thereof having olefinic unsaturation which is capable of polymerization by free radical polymerization

and

(ii) contacting the first surface of the substrate with the second surface of the 15 object.

2. The method of Claim 1 wherein the substrate is a roofing membrane.

3. The method of Claim 1 wherein the substrate and the object independently comprise a metal, a multilayer plastic, a multilayer composite, a thermoplastic, a thermoset; or combinations thereof.

20 4. The method of Claim 1 wherein the substrate and object are thermoplastic.

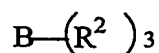
5. The method of Claim 1 wherein the substrate and the object independently comprise a polyolefin; acrylonitrile, butadiene and styrene terpolymer; polyvinyl chloride; chlorinated polyvinyl chloride; chlorinated/sulfonated polyethylene; ethylene/alpha-olefin/diene terpolymers; or blends thereof.

25 6. The method of Claim 1 wherein the substrate and the object comprise propylene polymers.

7. The method of Claim 1 wherein the substrate and the object comprise ethylene polymers.

30 8. The method of Claim 1 wherein the substrate is a first thermoplastic and the object is a second thermoplastic different from the first thermoplastic.

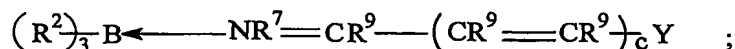
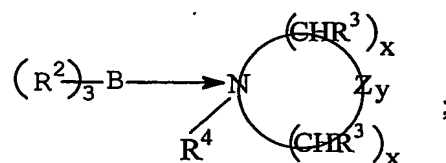
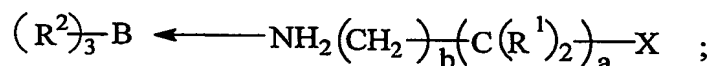
9. The method of Claim 1 wherein the organoborane amine complex includes an organoborane which has the structure

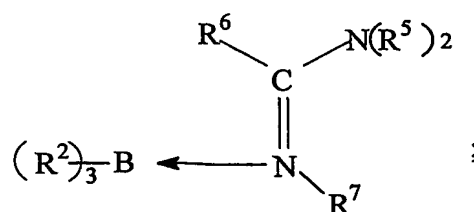


wherein B represents Boron; and  $R^2$  is separately in each occurrence a  $C_{1-10}$  alkyl,  $C_{3-10}$  cycloalkyl, or two or more of  $R^2$  may combine to form a cycloaliphatic ring.

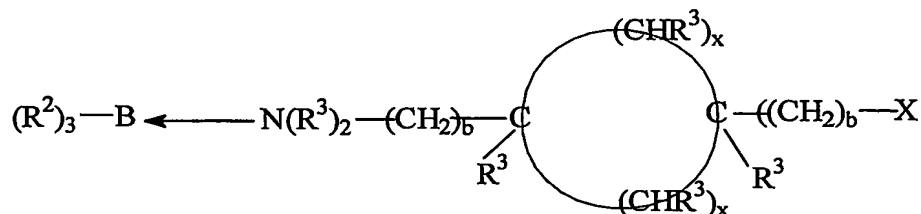
10. The method of Claim 1 wherein the organoborane amine complex includes  
 5 an amine which is a primary amine; a secondary amine; a polyamine having primary or secondary amines or both; ammonia; a polyoxyalkylene amine; a reaction product of a diamine and a difunctional compound having moieties which react with an amine, wherein the reaction product has terminal amine groups; an aryl amine; a heterocyclic amine; a compound having an amidine structural component; an aliphatic heterocycle  
 10 having at least one secondary nitrogen in the heterocyclic ring wherein the heterocyclic compound may also contain one or more additional secondary or tertiary nitrogen atoms, oxygen atoms, sulfur atoms, or double bonds in the heterocycle; an alicyclic compound having bound to the alicyclic ring one or more substituents containing an amine moiety; a conjugated imine or a mixture thereof.

15 11. The method of Claim 1 wherein the organoborane amine complex has the structure





or



wherein

B is boron;

- 5  $\text{R}^1$  is separately in each occurrence hydrogen, a  $\text{C}_{1-10}$  alkyl or  $\text{C}_{3-10}$  cycloalkyl;  
 $\text{R}^2$  is separately in each occurrence a  $\text{C}_{1-10}$  alkyl,  $\text{C}_{3-10}$  cycloalkyl or two or more of  $\text{R}^2$  may combine to form a cycloaliphatic ring structure;  
 $\text{R}^3$  is separately in each occurrence hydrogen, a  $\text{C}_{1-10}$  alkyl,  $\text{C}_{3-10}$  cycloalkyl or forms a double bond with a  $\text{R}^3$  or  $\text{R}^4$  on an adjacent atom;  
 10  $\text{R}^4$  is separately in each occurrence hydrogen,  $\text{C}_{1-10}$  alkyl,  $\text{C}_{3-10}$  cycloalkyl,  $\text{C}_{6-10}$  aryl or  $\text{C}_{6-10}$  alkaryl;  
 $\text{R}^5$  and  $\text{R}^6$  are separately in each occurrence hydrogen,  $\text{C}_{1-10}$  alkyl,  $\text{C}_{3-10}$  cycloalkyl,  $\text{N}(\text{R}^4)_2$  wherein  $\text{R}^7$  is separately in each occurrence hydrogen,  $\text{C}_{1-10}$  alkyl,  $\text{C}_{3-10}$  cycloalkyl or two or more of  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$  in any combination can combine to form a  
 15 ring structure which can be a single ring or a multiple ring structure and the ring structure can include one or more of nitrogen, oxygen or unsaturation in the ring structure;  
 $\text{R}^9$  is independently in each occurrence hydrogen,  $\text{C}_{1-10}$  alkyl or  $\text{C}_{3-10}$  cycloalkyl, Y,  $-(\text{C}(\text{R}^9)_2-(\text{CR}^9=\text{CR}^9))_c\text{-Y}$  or two or more of  $\text{R}^9$  can combine to form a ring structure, or  
 20 one or more of  $\text{R}^9$  can form a ring structure with Y provided the ring structure is conjugated with respect to the double bond of the imine nitrogen;  
 $\text{R}^{10}$  is separately in each occurrence  $\text{C}_{1-10}$  alkyl,  $\text{C}_{3-10}$  cycloalkyl or  $-(\text{C}(\text{R}^1)_2)_d\text{-W}$ ;  
 W is separately in each occurrence hydrogen,  $\text{C}_{1-10}$  alkyl or X;

X is  $OR^{10}$ ,  $SR^{10}$  or a halogen;

Y is independently in each occurrence hydrogen,  $SR^4$ ,  $N(R^4)_2$ ,  $OR^4$ ,  $C(O)OR^4$ , a halogen or an alkylene group which forms a cyclic ring with  $R^7$  or  $R^9$ ;

Z is separately in each occurrence oxygen or  $-NR^4$ ;

5 a is separately in each occurrence an integer of from 1 to 10;

b is separately in each occurrence 0 or 1, with the proviso that the sum of a and b should be from 2 to 10;

c is separately in each occurrence an integer of from 1 to 10;

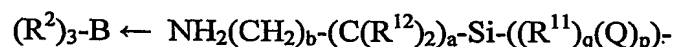
d is separately in each occurrence an integer of 1 to 4;

10 x is separately in each occurrence an integer of 1 to 10, with the proviso that the total of all occurrences of x is from 2 to 10; and

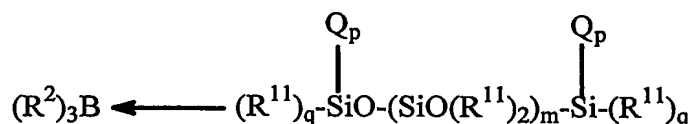
y is separately in each occurrence 0 or 1.

12. The method of Claim 1 where in the organoborane amine complex has the structure

15



or



20 wherein

B represents Boron;

$R^2$  is separately in each occurrence  $C_{1-10}$  alkyl,

$C_{3-10}$  cycloalkyl, or two or more of  $R^2$  may combine to form a cycloaliphatic ring;

Q is a hydrolyzable moiety;

25  $R^{11}$  is independently in each occurrence hydrogen, alkyl, alkoxy, alkenyl, alkyl amino or corresponds to the formula  $((CR^{14}H)_tO)_n-(NR^4)-(CH_2)_o-NH_2$  with the proviso that at least  $(R^{11})'$  is a primary amine leave this as is;

$R^{12}$  is independently in each occurrence hydrogen, alkyl, aryl, alkoxy, and may further contain one or more primary, secondary or tertiary amines;

30  $R^{14}$  is separately in each occurrence hydrogen or alkyl;

R<sup>4</sup> is hydrogen, C<sub>1-10</sub> alkyl, C<sub>6-10</sub> aryl or C<sub>7-10</sub> alkaryl;

a is a number of form 1 to 10;

b is a number of from 0 to 1;

m is separately in each occurrence a whole number of 1 or greater;

5 p is separately in each occurrence a number of from 1 to 3;

q is separately in each occurrence an integer from 1 to 2 wherein the sum of p and q on each silicon atom is 3;

n is separately in each occurrence an integer of 4 to 400;

o is separately in each occurrence an integer of 1 to 9 ; and

10 r is separately in each occurrence an integer of 2 or 4.

13. The method of Claim 1 wherein the adhesive further comprises: an effective amount of an isocyanate containing compound; one or more unpolymerized or partially polymerized compound having ring opening heterocyclic moieties and optionally a Lewis acid catalyst capable of initiating polymerization of the compound containing heterocyclic moieties; one or more compound, oligomer or prepolymer having siloxane groups and reactive moieties in its backbone capable of polymerization; one or more compound, oligomer or prepolymer having siloxane groups in its backbone which contain a moiety which when exposed to moisture forms an acid capable of decomplexing the organoborane amine complex; or mixtures thereof.

14. The method of Claim 1 wherein the adhesive comprises a polymerizable acrylate monomer.

15. The method of Claim 1 wherein the adhesive has a VOC emission of less than 650 g/l.

25 16. The method of Claim 1 wherein the adhesive has a VOC emission of less than 270 g/l.

17. A method to repair a new or existing substrate, object, or substrate/object joint having one or more surface in need of repair comprising the steps of

(i) applying an effective amount of a curable adhesive composition to the surface(s) in need of repair, a repair patch or both the surface in need of repair and the repair patch, wherein the adhesive comprises

(a) an effective amount of a organoborane amine complex initiator and

(b) one or more monomers, oligomers, polymers or mixtures thereof having olefinic unsaturation which is capable of polymerization by free radical polymerization.

and

5 (iii) bonding a repair patch to the surface in need of repair.

18. The method of claim 1 wherein the adhesive further comprises a liquid.

19. The method of claim 18 wherein the liquid comprises water.

10 20. A substrate having a first surface bonded to an object having a second surface, wherein the bond comprises:

(i) an effective amount of a curable one or two part adhesive composition to the first surface of the substrate, the second surface of the object or to both surfaces, wherein the adhesive comprises

15 (a) an effective amount of a organoborane amine complex initiator and

(b) one or more monomers, oligomers, polymers or mixtures thereof having olefinic unsaturation which is capable of polymerization by free radical polymerization.

20 21. The method of claim 1 further comprising the step of applying an effective amount of pressure to the substrate /adhesive/object in order for the adhesive to cure.

22. The method of claim 1 further comprising the step of exposing the adhesive to air for a sufficient amount of time to develop green strength of the adhesive prior to step (ii).

25 23. The method of Claim 1 wherein the curable adhesive compound is a one part compound.

30 24. The method of Claim 1 wherein the curable adhesive compound is a two part compound.

25. The method of claim 1, further comprising the step of ensuring that the first and second surfaces contain substantially no water prior to step (i).

26. The method of claim 1, further comprising the step of ensuring that the first and second surfaces are substantially oil-free prior to step (i).